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(54) EASILY WATER-DISPERSIBLE CARBON BLACK AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing an easily water-dispersible carbon black having an excellent dispersibility, i.e., easily dispersible in water and capable of stably maintaining the dispersion state for a long term.

SOLUTION: This carbon black has a surface modified by oxidation and a heat of wetting with water of 0.1 J/m2 or higher and is produced by subjecting a carbon black to wet oxidation with a peroxodisulfate, peroxodisulfate and an acid, or a halogenic acid salt and an acid followed by separation by filtration and purification, thus modifying the surface to give it a heat of wetting with water of 0.1 J/m2 or higher. Pref., oxidation-active sites are formed on the carbon black surface by gas-phase oxidation before the wet oxidation.

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CLAIMS

[Claim(s)]
[Claim 1] Easy water dispersible carbon black which is carbon black in which surface treatment was carried out by oxidation treatment, and is characterized by equipping the water heat of wetting with a two or more 0.1 J/m property.
[Claim 2] The manufacture approach of the easy water dispersible carbon black characterized by the thing which carried out wet oxidation processing of the carbon black using the pel oxo-disulfuric acid salt or the pel oxo-disulfuric acid salt, the acid, or a halogen acid salt and an acid, and which back filtration separation is carried out, purification processing is subsequently carried out, and the water heat of wetting does to two or more 0.1 J/m for surface treatment.
[Claim 3] The manufacture approach of the easy water dispersible carbon black according to claim 2 which carries out wet oxidation processing after carrying out vapor phase oxidation of the carbon black beforehand and forming the oxidization active spot in a carbon black front face.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to easy water dispersible carbon black excellent in the dispersibility to the water suitably used as black system water-color-ink pigments, such as for example, an ink pigment for ink jet printers, a common water-color-ink pigment, and a pigment for electrodeposition coating, and its manufacture approach.
[0002]
[Description of the Prior Art] Since wettability [as opposed to water at hydrophobicity] of carbon black is low, it is very difficult to make it distribute underwater to stability by high concentration. This originates in that there are very few functional groups of hydrophilic properties, such as a hydrogen content functional group with high compatibility with the water molecule which exists in a carbon black front face. therefore -- the case where distribute carbon black underwater as a black system pigment, and it is used as watercolor pigment ink etc. -- the front face of carbon black -- it is necessary to reform description and to aim at water-dispersion improvement
[0003] Watercolor pigment ink begins a writing implement, and it is observed as recording ink especially for ink jet printers etc. in recent years, for example, the recording ink for ink jet with which an aquosity medium, polyoxyethylene styryl phenyl ether, and the diameter of a primary particle are characterized by containing the carbon black 40-120ml / 100g, and whose pH 20-40nm and DBP oil absorption are 7.0 or more is proposed by JP,3-97770,A. By using polyoxyethylene styryl phenyl ether as a dispersant, improvement in the preservation stability of recording ink is aimed at, a commercial item is used for target carbon black, and it does not have the intention of this at all about the denaturation of carbon black.
[0004] Moreover, improving the underwater dispersibility of carbon black is known for many years by oxidizing carbon black and forming the functional group of a hydrophilic property in a front face. For example, to JP,48-18186,A, carbon black is oxidized in the water solution of the following ** halogen acid salt, and in more nearly subsequently than the system of reaction carrying out separation uptake of the oxidization carbon black, the manufacturing method of the water-dispersion refining carbon black to which the manufacture approach of the oxidization carbon black characterized by washing by the organic solvent is characterized by carrying out low-temperature-oxidation plasma treatment of the carbon black to JP,57-159856,A again is proposed.
[0005] Furthermore, it sets in the watercolor pigment ink which contains water and carbon black in JP,8-3498,A, It sets to the manufacture approach of the watercolor pigment ink in which this carbon black has the surface activity hydrogen content of 1.5 or more mmol/g, and the watercolor pigment ink containing water and carbon black, and is (a). The process which obtains acid carbon black, and (b) The manufacture approach of the watercolor pigment ink which includes the process which oxidizes said acid carbon black further with the following ** halogen acid salt underwater is proposed. Moreover, in JP,8-319444,A, they are the oil absorption of 100ml / 100g. The manufacture approach of the watercolor pigment ink which includes process; which oxidizes this carbon black using process; and the following

** halogen acid salt which carry out differential powder of the following carbon black into an aquosity medium is indicated.
[0006] In above-mentioned JP,8-3498,A and above-mentioned JP,8-319444,A, by oxidizing carbon black and making the functional group containing many active hydrogen which is the functional group of a hydrophilic property form in a front face, water-dispersion is good and obtains watercolor pigment ink excellent in prolonged distributed stability. However, in the process which carbon black distributes underwater, it is difficult to achieve a function with the important amount of functional groups of the hydrophilic property which exists in the contact interface of a carbon black front face and a water molecule, and to only judge the quality of dispersibility exactly in the amount of functional groups per carbon black unit weight.
[0007] then, it be carbon black in which this invention person considered as the new technique of evaluate the quality of dispersibility exactly, and refining be carried out by oxidation treatment paying attention to the amount of hydrogen content functional groups which exist in per carbon black unit surface area, and the development proposal of the easy water dispersible carbon black to which the amount of total of a carboxyl group and hydroxyl be characterize by be two or more 3microeq/m per unit surface area among the hydrogen content functional groups which exist in a front face, and its manufacture approach be made (Japanese Patent Application No. No. 332405 [nine to]).
[0008]
[Problem(s) to be Solved by the Invention] this invention person found out that the underwater heat of wetting of carbon black was effective as a scale not only including the amounts of hydrophilic hydrogen content functional groups, such as a carboxyl group which exists in a carbon black front face, and hydroxyl, but other factors which evaluates the function of a hydrophilic property synthetically, as a result of advancing research further based on the above-mentioned technique.
[0009] It is in this invention offering the easy water dispersible carbon black which was developed based on this knowledge, and that object excels [easy water dispersible carbon black] in underwater dispersibility ability, for example, can be suitably used as black system water-color-ink pigments, such as an ink pigment for ink jet printers, a common water-color-ink pigment, and a pigment for electrodeposition coating, and its manufacture approach.
[0010]
[Means for Solving the Problem] The easy water dispersible carbon black concerning this invention for attaining the above-mentioned object is carbon black in which surface treatment was carried out by oxidation treatment, and is characterized by equipping the water heat of wetting with a two or more 0.1 J/m property on a configuration.
[0011] Moreover, the manufacture approach is characterized by the thing which carried out wet oxidation processing of the carbon black using the pel oxo-disulfuric acid salt or the pel oxo-disulfuric acid salt, the acid, or a halogen acid salt and an acid and which back filtration separation is carried out, purification processing is subsequently carried out, and the water heat of wetting does to two or more 0.1 J/m for surface treatment on a configuration. In addition, before carrying out wet oxidation processing, it is desirable to carry out vapor phase oxidation beforehand and to form the oxidation active spot in a carbon black front face.
[0012]
[Embodiment of the Invention] Although especially the colloidal property of target carbon black is not limited in this invention, in order for a carbon black front face to fully be wet by the water molecule in the process which carbon black distributes underwater and to maintain a stable distributed condition underwater, the area in contact with a water molecule comes out enough, and a certain thing is required. That is, when the specific surface area of carbon black is small, the area of the interface in contact with a water molecule will also decrease, and dispersibility will fall. Moreover, since the condensation unit in the condition of having distributed underwater will also become large if the structure of carbon black is high, it becomes easy to sediment by re-condensation at the time of the distribution over a long period of time.
[0013] Furthermore, if the specific surface area of carbon black becomes small when it uses as a black

pigment for water color ink, the Japanese lacquer blackness of printing will become low. Moreover, to use for an ink pigment, a black ink pigment, etc. for ink jet printers, it is required to have regurgitation stability, paper fixation concentration (paper printing concentration), etc. of ink with sufficient balance. For the value of nitrogen adsorption specific surface area (N2SA), the value of DBP oil absorption is [target carbon black] 70ml / 100g more than 50m2/g at these points to this invention. It is desirable to set it as the following properties.

[0014] The underwater dispersibility of carbon black becomes possible [judging a wettability quality synthetically by the size of the heat generated when a carbon black particle front face contacts water, since it is greatly influenced by the wettability to the water of a carbon black particle front face, i.e., the water heat of wetting,]. Then, the easy water dispersible carbon black of this invention is characterized by the point of having set the value of the water heat of wetting which converted into the calorific value per carbon black unit surface area the heating value generated when carbon black is supplied underwater as the two or more 0.1 J/m value.

[0015] In addition, the value from which the water heat of wetting was obtained by the following measuring method is applied.

The measuring method of the water heat of wetting; after ****(ing) the carbon black sample which is equivalent to the surface area of 2 about 10m from the value of nitrogen adsorption specific surface area (N2SA) in glass ampul and deaerating under the temperature of 105 degrees C, and the vacuum of 1x10-5Torr for 3 hours, ampul is opened under a vacuum and a test portion is prepared. measurement -- a twin type -- constant temperature -- it carried out on conditions with a water temperature of 30 degrees C using the wall calorimeter [the product made from Tokyo Science and engineering, and a TIC-2C mold].

[0016] The easy water dispersible carbon black of this invention can manufacture carbon black by [which carried out wet oxidation processing using the pel oxo-disulfuric acid salt or the pel oxo-disulfuric acid salt, the acid, or a halogen acid salt and an acid] carrying out back filtration separation and subsequently carrying out purification processing.

[0017] As a pel oxo-disulfuric acid salt used as an oxidizer, an alkali-metal salt, ammonium salt, etc. of persulfuric acid are used, and 0.5Ns or more of concentration are desirable. Moreover, when using the mixed solution of a pel oxo-disulfuric acid salt and an acid, the concentration of a pel oxo-disulfuric acid salt is 0.3Ns or more, and as for the concentration of an acid, it is desirable to set it as 0.5Ns or more. In addition, a hydrochloric acid and a sulfuric acid are used as an acid, the function of phosphoric acid as an acid is [ionization degree is small,] low, and since steric hindrance is caused that it is easy to form a nitro group in a carbon black front face and dispersibility falls, a nitric acid is not desirable.

[0018] not only a halogen acid salt but a ** halogen acid salt is used for the halogen acid salt used as an oxidizer -- having -- as a halogen -- chlorine, an iodine, a bromine, and a fluorine -- although all are used, chlorine is used preferably, and an alkali-metal salt and ammonium salt are used as a salt. It is strong with acidity, and at neutrality and alkalinity, since it is remarkably weak, as an oxidizer, the mixed solution of a halogen acid salt and an acid is used, and as for the oxidation effectiveness in the water solution of a halogen acid salt, a hydrochloric acid or a sulfuric acid is preferably used for an acid. In addition, the concentration of 0.5Ns or more and an acid has [the concentration of a halogen acid salt] desirable 0.5Ns or more.

[0019] While mixed distribution is carried out and wet oxidation processing stirs carbon black at a proper rate to the mixed solution of the pel oxo-disulfuric acid salt, pel oxo-disulfuric acid salt, and acid which were suitably adjusted to concentration, or the mixed solution of a halogen acid salt and an acid, predetermined oxidation treatment is performed by controlling processing temperature, the processing time, etc. suitably.

[0020] In addition, if vapor phase oxidation is beforehand carried out with ozone, ozone content air, etc. and the oxidation active spot (oxidation site) is formed in the carbon black front face, wet oxidation processing can be advanced more smoothly. Therefore, after carrying out vapor phase oxidation beforehand and forming the oxidation active spot, it is desirable to perform wet oxidation processing. Vapor phase oxidation is in the condition which carried out humidity to the condition or water which

dried carbon black, and is performed by carrying out time amount contact suitably with ozone and ozone content air.

[0021] Thus, rinsing clearance of the oxidizer which fully washed the carbon black which carried out wet oxidation processing with pure water after filtration separation was carried out from the oxidizer solution, and has adhered is carried out. furthermore, the electrodialysis in order to refine to a high grade, after having put in carbon black into pure water, adjusting pH to 5-8 and distributing carbon black or ultrafiltration membrane, and loose R.O etc. -- purification processing is carried out by separating residual salt by the demarcation membrane. Thus, the easy water dispersible carbon black by which surface treatment of the water heat of wetting was carried out to two or more 0.1 J/m is manufactured.

[0022]

[Example] Hereafter, the example of this invention is concretely explained as contrasted with the example of a comparison.

[0023] Example 1 nitrogen adsorption specific-surface-area (N2SA) 135m2/g, and DBP oil absorption 56 ml / 200g of 100g carbon black samples It put into the ozone place hairdressing machine, and vapor phase oxidation was carried out in ordinary temperature for 1 hour using the ozonizer [the product made from Japanese Ozone, and IOT-4A6] to the bottom of the condition of generated-voltage 200V and ozone yield 18 g/h. This carbon black 150g that carried out vapor phase oxidation After making water distribute the carbon black which was obtained with the reaction temperature of 60 degrees C by carrying out wet oxidation processing for 10 hours, and subsequently carrying out filtration separation and by which wet oxidation processing was carried out, having put in into 3000ml of pel oxo-disulfuric acid ammonium 1.5N solutions, and stirring (300rpm), the sodium-hydroxide water solution (concentration of 0.5Ns) neutralized, and the carbon black dispersing element was obtained. Furthermore, it dried, after removing impurities, such as salts which carry out purification processing of this carbon black dispersing element by ultrafiltration membrane [the Asahi Chemical Industry Co., Ltd. make, APH-1010, cut-off-molecular-weight 50000], and remain. Thus, the easy water dispersible carbon black which carried out surface treatment was manufactured.

[0024] The 200g of the same carbon black samples as example 2 example 1 It dried, after carrying out humidity with 220ml pure water and carrying out ozonate on the same conditions as an example 1. Subsequently, this carbon black 150g After carrying out wet oxidation processing with the reaction temperature of 100 degrees C for 10 hours, having put in into 0.5 Ns of sodium chlorates, and 3000ml of mixed solutions of 1 N of sulfuric acids, and stirring (300rpm), it dissociated [filtration-] and processed [purification-] by the same approach as an example 1, and the front face manufactured the easy water dispersible carbon black by which refining was carried out.

[0025] 150g of carbon black samples which carried out vapor phase oxidation like example 3 example 1 After carrying out wet oxidation processing with the reaction temperature of 60 degrees C for 10 hours, having put in into 3000ml of pel oxo-disulfuric acid ammonium 1.0N water solutions, and stirring (300rpm), it dissociated [filtration-] and processed [purification-] by the same approach as an example 1, and the front face manufactured the easy water dispersible carbon black by which refining was carried out.

[0026] The carbon black which the sodium-chlorate water solution with a concentration of 0.5 Ns was used as example of comparison 1 oxidizer, and also reformed the front face by the same approach as an example 2 was manufactured.

[0027] The 200g of the same carbon black samples as example of comparison 2 example 1 It dried, after carrying out humidity with 220ml pure water and carrying out ozonate on the same conditions as an example 1, and the carbon black which reformed the front face was manufactured.

[0028] The 150g of the same carbon black samples as example of comparison 3 example 1 Tales-doses addition of the alpha olefin sulfonic-acid system dispersant [the LION make and Lipolan PB-800] is carried out, and it is 700g of pure water. After carrying out grinding processing with a ball mill in addition for 48 hours, it filtered and dried and the carbon black which carried out surface treatment was prepared.

[0029] Thus, in order to measure the water heat of wetting of the obtained carbon black and to evaluate

the dispersibility ability to water, the dispersion liquid which water was made to distribute carbon black and were adjusted to 20% of the weight of distributed concentration were produced, and it examined by the following approach. The obtained result was shown in a table 1.
** warming -- put a stability sample in a well-closed container, and observe about the viscosity change for one to four weeks in a 70-degree C attemperator. Measurement of viscosity was measured using the rotational-vibration type viscometer [Yamaichi Electronics make and VM-100 A-L].
** The frozen freeze-thaw-stability sample was put in the well-closed container, and three cycles of viscosity change when freezing and thawing at -20 degrees C - 25 degrees C were measured.
** a particle diameter measurement sample and warming -- it measured using the heterodyne laser Doppler system particle-size-distribution measuring device [micro truck company make and UPA model9340] about the particle diameter of the sample which performed the stability test. If a laser beam is applied to the particle which is carrying out Brownian motion into suspension, the frequency of the scattered light will modulate this measuring device by the Doppler effect. The violence of Brownian motion, i.e., particle diameter, is measured from the modulation degree of the frequency.
[0030]
[A table 1]

		実施例			比較例		
		1	2	3	1	2	3
水湿潤熱 (J/m²)		0.24	0.21	0.12	0.087	0.056	0.27
粘度 (cp)	初期粘度	2.82	2.71	3.12	6.54	3.55	2.12
	70℃ 1 W経過後	2.82	2.71	3.12	6.66	ゲル化	2.11
	70℃ 2 W経過後	2.81	2.69	3.11	6.78	——	2.11
	70℃ 3 W経過後	2.81	2.69	3.11	7.45	——	2.10
	70℃ 4 W経過後	2.80	2.69	3.11	8.12	——	2.09
平均粒径 (nm)	初期粒径	69.5	68.4	71.5	154.2	162.1	67.1
	70℃ 1 W経過後	69.2	68.2	71.2	155.6	測定不	67.1
	70℃ 2 W経過後	69.1	68.1	70.9	156.2	可	66.9
	70℃ 3 W経過後	68.4	67.9	70.8	158.1	——	66.8
	70℃ 4 W経過後	68.2	67.4	70.4	160.2	——	66.7
最大粒径 (nm)	初期粒径	171.9	168.5	182.1	464.2	478.2	169.4
	70℃ 1 W経過後	171.8	168.4	182.1	465.1	測定不	169.3
	70℃ 2 W経過後	171.8	168.4	181.9	466.2	可	168.7
	70℃ 3 W経過後	171.7	168.3	181.9	467.2	——	168.4
	70℃ 4 W経過後	171.6	168.3	181.7	468.5	——	168.2
冷凍解凍 (cp)	1サイクル	2.81	2.72	3.13	7.45	6.12	分離
	2サイクル	2.81	2.72	3.12	8.21	6.54	〃
	3サイクル	2.81	2.72	3.11	8.54	7.42	〃

[0031] Viscosity tends to decrease also after one week - four week progress under the condition that the dispersion liquid of the examples 1-3 which made the carbon black in which oxidized carbon black and the water heat of wetting carried out surface treatment to the two or more 0.1 J/m value from the result of a table 1 distribute underwater at 20% of the weight of a rate were warmed by 70 degrees C, and the particle diameter of the carbon black in dispersion liquid is also decreasing, and it turns out that the stable distributed condition is maintained. On the other hand, it is in a thickening inclination from one

week in the condition of having warmed at 70 degrees C, re-condensation of carbon black progressed remarkably, and the dispersion liquid of the examples 1 and 2 of a comparison which distributed underwater the carbon black in which the value of the water heat of wetting is less than 0.1 J/m2 even if it oxidizes have also produced gelation. moreover -- the dispersion liquid of the example 3 of a comparison which the surface active agent was made to stick to a carbon black front face without oxidizing, and reformed the value of the water heat of wetting to two or more 0.1 J/m -- 70 degrees C -- warming -- in the condition, although the increment in thickening or mean particle diameter, or the diameter of grain of maximum size was not observed, when the frozen thawing experiment was conducted, the surface active agent carried out desorption of it, and it was divided into carbon black and water. Moreover, by carrying out wet oxidation processing, using a pel oxo-disulfuric acid salt, a pel oxo-disulfuric acid salt, and an acid as an oxidizer shows that the surface treatment of the water heat of wetting which is easy water dispersible carbon black of this invention can be carried out to a two or more 0.1 J/m value.

[0032]

[Effect of the Invention] The easy water dispersible carbon black which was excellent in the distributed engine performance which can distribute easily underwater according to this invention, and can continue at a long period of time, and can maintain a stable distributed condition, and its manufacture approach are offered as above. Therefore, if it is used as recording ink for ink jet printers by using the easy water dispersible carbon black of this invention as a black system water-color-ink pigment, it excels in regurgitation stability and paper fixation concentration, printing grace, lightfastness, preservation stability, etc. can obtain good ink. Therefore, it is very useful as easy water dispersible carbon black suitably used including the ink pigment for ink jet printers as black system water-color-ink pigments, such as a general water-color-ink pigment and a pigment for electrodeposition coating. Moreover, according to the manufacture approach of this invention, it becomes possible to manufacture easy water dispersible carbon black equipped with this outstanding dispersibility ability.

[Translation done.]